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CERAMICS FROM MINING BY-PRODUCTS AND ALUMINA PRODUCTION WASTES

V. A. Sviderskii,¹ S. V. Strashnenko,¹ and L. P. Chernyak¹

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The possibility of obtaining chemically stable ceramics in plastic molding from pastes based on comprehensive use of mining by-products (plagioporphry, quartz-biotite shale), alumina production wastes (red mud), and polymineral clay was demonstrated. The mechanism of enhancing paste sintering on addition of finely disperse grog-flux and increasing the alkali resistance of the material (to 95%) in molding of the crystalline hematite – anorthite – quartz system was examined.

Development of the ceramics industry is due to practical implementation of the achievements of scientific and technical progress in expanding the raw materials base and improving product performance properties.

High-melting hydromica–kaolinite clays are the basic component of industrial pastes for fabrication of construction ceramics, including chemically resistant ceramics [1, 2]. However, the amount and reserves of quality high-melting clays are limited, which has caused the scarcity and price of these clays to increase due to the constantly increasing demand for them. At the same time, there are many polymineral clay deposits, and individual branches of industry are constantly accumulating important volumes of mining by-products and production wastes, and efficiently utilizing

them in ceramics technology requires special process developments (USSR Inventor's Certificate No. 1655948) [3, 4].

Kostomuksha Mining-Concentration Combine (KMCC) (Karelian Pellet Co.) annually extracts up to 2 million m³ of quartz–feldspar rock in working an iron ore deposit, and in non-ferrous metallurgy, more than 1.5 million tons of wastes — red mud — is formed annually in processing bauxites for silica.

We investigated ceramics from pastes with comprehensive utilization of technogenic (red mud) and natural (mining by-products and polymineral clay) feedstock (Table 1), the dependence of its properties on the composition of the raw material and pastes, the degree of completion of sintering, and the parameters of the structure formed after firing.

Red mud is distinguished by a high iron oxide content at a low concentration of SiO₂, and its phase-mineral composition is represented by goethite, hematite, rutile, and hydrargillite crystals. Polymineral Meshkovsk clay contains much

¹ Kiev Polytechnic Institute National Technical University of Ukraine, Kiev, Ukraine; Ukrstroimaterialy Corporation, Kiev, Ukraine.

TABLE 1

Test	Mass content, %									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	calcination loss
Clay:										
Artem	71.95	16.53	2.06	0.54	1.51	0.54	0.48	0.34	0.45	5.20
Meshkovo	64.08	11.21	4.15	0.62	6.04	2.55	0.27	0.62	1.91	9.04
NGZ (Nikolaev Alumina Refinery) red mud	12.40	10.36	58.64	2.36	1.21	1.02	0.22	3.50	0.20	10.80
Plagioporphry	70.01	15.52	1.99	0.14	3.65	0.72	0.39	4.99	0.92	0.93
Shale:										
talchlorite	39.56	6.23	10.12	0.40	5.31	24.06	1.24	0.05	1.58	11.31
quartz-biotite	46.98	9.44	9.60	0.50	6.00	9.88	0.09	0.48	4.37	8.25

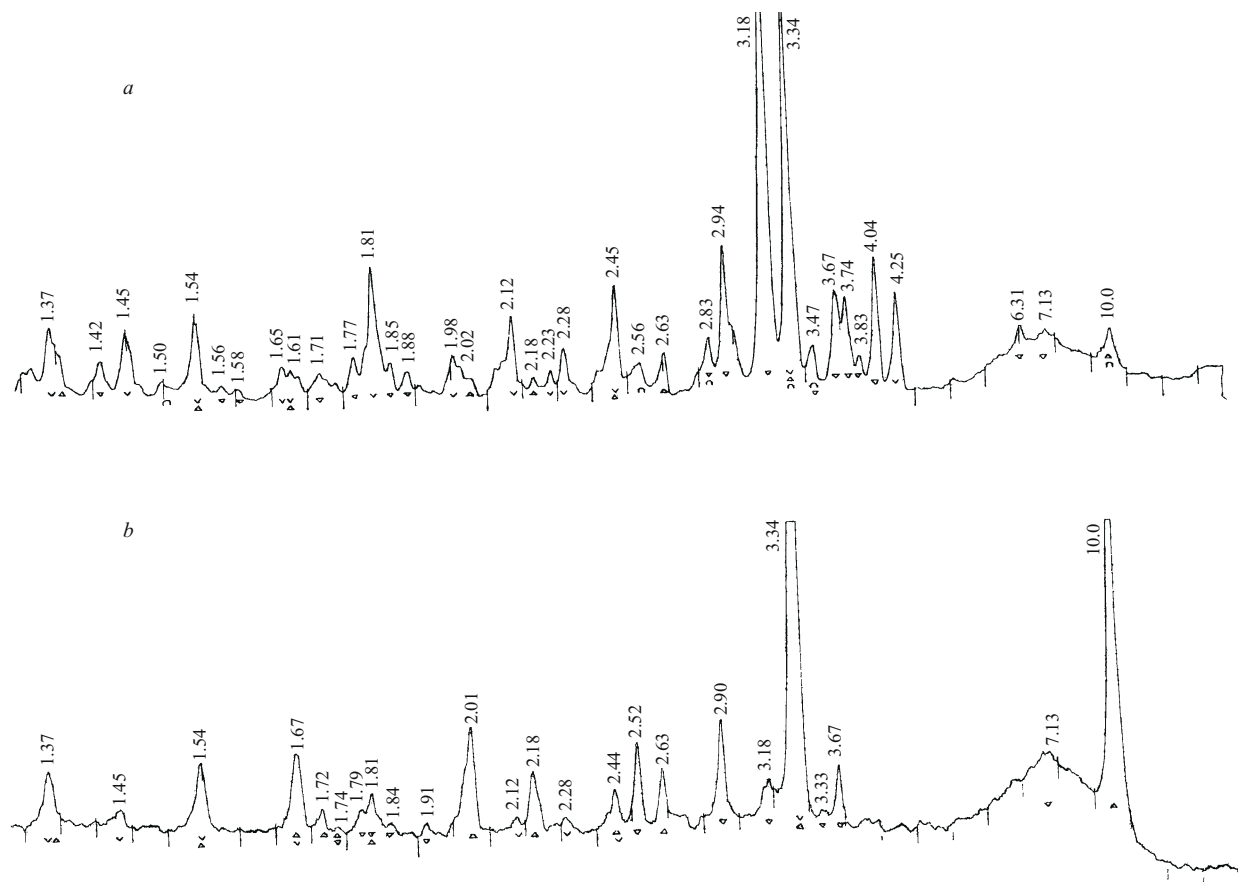


Fig. 1. X-ray patterns of a sample of plagioporphry (a) and quartz-biotite shale (b): (v) quartz; (∇) plagioclase; (Δ) biotite; (○) muscovite.

more alkaline and alkaline-earth oxides ($R_2O + RO$), iron oxides, and less Al_2O_3 than high-melting hydromica-kaolinite clay.

KMCC mining by-products differ significantly in chemical-mineral composition. Plagioporphry (plagioclase porphyry) most satisfies the criteria for selecting raw material for modern construction ceramics technology (high Al_2O_3 and alkali oxide content, minimal iron oxide content). Quartz-biotite shale is inferior to plagioporphry (lower Al_2O_3 content and high iron oxide content), but it is also of interest, since it is characterized by an important content of alkali and alkaline-earth oxides.

The mining products investigated were distinguished by developed crystalline phases, which is due to their genesis at the high temperatures of volcanic activity. Plagioporphries contain (%): 50 – 70 plagioclase (primarily oligoclase and anorthite), 25 – 35 quartz, 15 biotite, and 1 – 10 muscovite.² In addition to quartz, quartz-biotite shale contains 15 – 35% biotite and 10% plagioclase (Fig. 1).

The experimental pastes (Table 2) are mixtures of technogenic and natural raw material. At a constant clay content, the red mud content varied from 75.0 to 37.5% and the content of mining by-products varied from 15.0 to 37.5%.

² Here and below: mass content.

TABLE 2

Paste	Mass content, %				Chemical composition, %					
	red mud	polyminerall clay	plagioporphry	quartz-biotite shale	SiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
K	75.0	25	—	—	25.32	45.02	2.42	1.40	2.78	0.63
K1	60.0	25	7.5	7.5	32.23	44.99	2.96	1.51	2.67	1.00
K2	45.0	25	15.0	15.0	39.15	29.00	3.50	2.69	2.56	1.37
K3	37.5	25	18.7	18.7	42.61	25.20	3.76	3.01	2.50	1.55

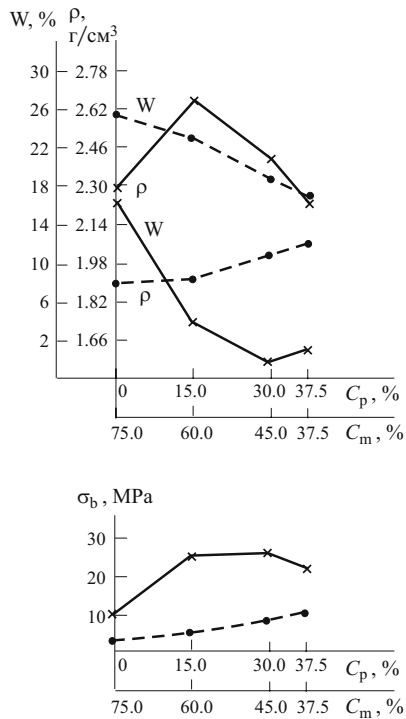


Fig. 2. Density ρ , water absorption W , and bending strength σ_b of ceramic as a function of red mud content C_m , mining by-products C_p , and firing temperature (1150 and 1200°C — dashed and solid lines, respectively).

The chemical composition of the pastes also varied correspondingly with respect to the total content (%): 25 – 43 SiO₂, 25 – 45 Fe₂O₃, 7 – 11 alkali and alkaline-earth oxides (R₂O + RO).

It was found that use of a mixture of plagioporphyry and quartz-biotite shale (PC) significantly intensifies sintering of ceramic pastes, and the magnitude of the effect is a function of the concentration of this mixture and the degree of firing (Figs. 2 and 3).

After firing at 1150°C, the maximum intensification of sintering of the ceramic (9.1% decrease in water absorption, 4-fold increase in bending strength, and 0.16 sec/cm³ increase in density) was attained at the same 30.0% PC and red mud content, paste K3, and when the firing temperature increased to 1200°C, at a 30.0% PC mixture and 45.0% red mud content, paste K2 (15.5% decrease in water absorption, increase in density by 0.13 g/cm³, and bending strength by 3 times).

In the maximum firing temperature range of 1175 – 1200°C, the ceramic from paste K2 was characterized by 0.7 – 0.9% water absorption, density of 2.42 – 2.43 g/cm³, and bending strength of 26 – 28 MPa.

The observed effect of mining by-product additives on the chemical stability of the ceramic is experimentally important. It was found that after firing at 1200°C, the material from pastes K1 – K3 had acid resistance of 97.4 – 98.0% and alkali resistance of 91.5 – 94.8%. Equally high acid and alkali resistance indexes were also obtained when paste K2

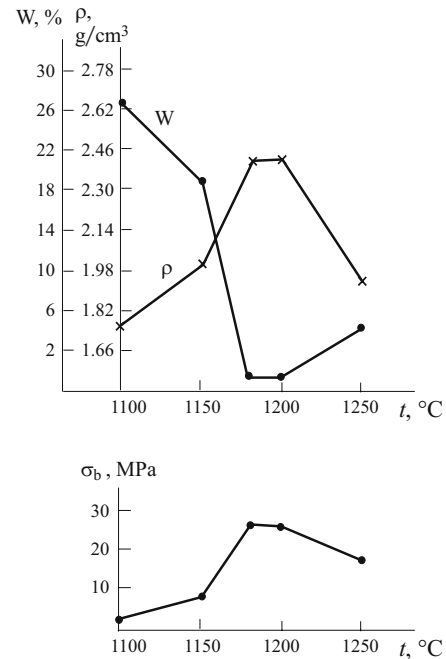


Fig. 3. Density ρ , water absorption W , and bending strength σ_b of ceramic from paste K2 as a function of the firing temperature.

with a 30% plagioporphyry and quartz-biotite mixture content was used (Table 3).

As the results of the studies show (Table 4), at the same degree of firing, the ceramic from the experimental pastes containing KMCC mining by-products is distinguished by significant lower open and total porosity, a larger fraction of closed pores, and correspondingly important development of the glass phase. This tendency is enhanced with an increase in the concentration of these components, and when paste K2

TABLE 3

Paste*	Acid resistance, %	Alkali resistance, %
K	94.24	93.55
K1	97.41	92.27
K2	97.46	94.84
K3	97.98	91.50

* Firing temperature of 1200°C.

TABLE 4

Paste*	Porosity, %		Fraction of closed pores, %
	open	total	
K	37.72	39.63	4.82
K1	10.68	21.93	51.30
K2	2.19	25.23	91.32
K3	3.79	28.52	86.71

* Firing temperature of 1200°C.

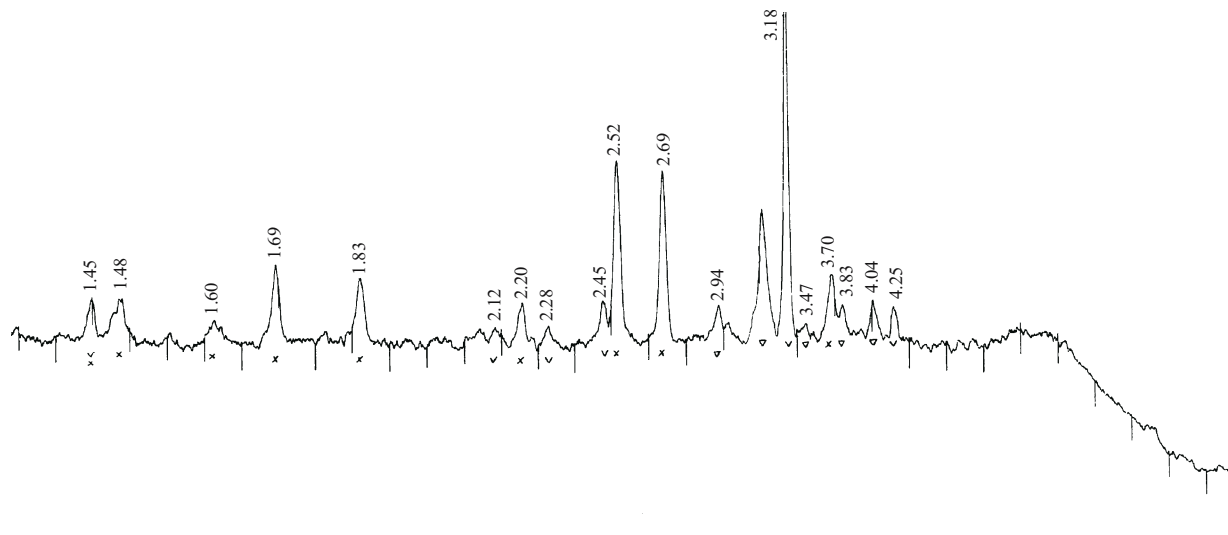


Fig. 4. X-ray pattern of ceramics from paste K2 after firing at 1200°C: v) quartz; x) hematite; ∇) anorthite.

was used, the fraction of closed pores reached 91% and the amount of open pores decreased to 2%.

The x-ray structural analysis revealed the features of the crystalline phases of the ceramics made from the experimental pastes after firing. In contrast to the hydromica-kaolinite clay ceramic, characterized by development of quartz – mullite and quartz – mullite – cristobalite crystal systems [5], the ceramics from the experimental pastes differed by the development of a hematite – anorthite – quartz crystal system (Fig. 4). The amount of anorthite increased significantly with an increase in the concentration of this mixture.

A process scheme using methods of slip preparation of pastes and plastic molding was developed for production of ceramic ware (pipes, acid-resistant materials, road paving elements). An aqueous suspension of finely disperse ($\leq 60 \mu\text{m}$) mining by-products was fed in to moisten the mixture of other components in a twin-shaft mixture, ensuring:

homogeneity and formation of a complete coagulation structure in the paste preparation and molding stages;

intensification of sintering in firing.

Enhancement of sintering of the ceramics made from the experimental pastes is due to the indicated features of the chemical and mineral composition and the high dispersion of the components.

Preliminary milling of the mixture of mining by-products increased their effective specific surface area and degree of surface defectiveness, while addition of the mixture to the paste increased the number of contacts of particles of the disperse phase, area of active interphase surface area and the free surface energy content as the thermodynamic grounds for activation of sintering [6 – 8]. Diffusion of the chemical components increased on the contact boundary of the finely disperse particles with development of a liquid phase that causes compacting of the particles due to surface tension energy and formation of crystalline phases [9]. The observed genetically developed crystalline phases of the mining

by-products is an important factor in structure formation, which determines the properties of the ceramics from the developed pastes.

Improving the physicomechanical and performance properties of ceramics is thus a function of the features of structure formation: increasing the density and decreasing the porosity is a function of increasing the dispersion of the components and amount of glass phase, increasing the strength is a function of the dispersion of the developed hematite – anorthite – quartz crystal system in the glass phase, and increasing the chemical resistance is a function of decreasing the open porosity and specific contact surface area with the aggressive medium, as well as the phase composition.

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